UDC 669.2/.8
DOI: 10.53297/18293395-2025.2-20

HYDROMETALLURGICAL PROCESSING OF CHALCOPYRITE CONCENTRATES FOR COPPER, GOLD, AND SILVER RECOVERY

A.M. Hovhannisyan, D.G. Vardanyan

National Polytechnic University of Armenia

The present work describes the specific features of hydrometallurgical processing of copper concentrates. The characteristics of heap leaching, in-situ (vat) leaching, and bioleaching processes are presented. In industrial copper concentrates, copper is predominantly present in the form of chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S), while iron occurs mainly as pyrite (FeS_2). The optimal technological conditions for concentrate leaching have been outlined with the aim of achieving maximum recovery of valuable metals. It is demonstrated that the selection of an appropriate processing scheme must be based on the mineralogical composition of the feed, the distribution of the associated metal phases, and the concentration of recoverable components.

For sulfur-rich copper concentrates, direct chloride leaching is identified as the most efficient method, characterized by high copper dissolution rates, strong selectivity, and favorable operating conditions. Under optimized parameters, copper fully transitions into solution in the form of monovalent copper chloride, which is subsequently processed to obtain high-purity metallic copper.

Iron recovery from the insoluble oxide residues is carried out through a controlled two-stage hydrogen reduction process, resulting in metallic iron powder suitable for industrial applications. The final oxide tailings, enriched with gold and silver, undergo cyanide leaching followed by precipitation and electrochemical treatment to produce a high-quality doré alloy.

The proposed integrated technological scheme ensures comprehensive utilization of the feedstock and high recovery efficiencies for both base and precious metals. Moreover, the closed-cycle nature of chloride leaching and the reduction of secondary waste enhance the environmental safety and overall sustainability of the process.

Keywords: copper sulfide concentrate, mineralogical composition, leaching, recovery.

Introduction. Modern hydrometallurgical technological cycles for the direct extraction of copper from ores generally consist of three main stages (processes): leaching, solvent extraction, and electrowinning. The leaching process involves the transfer of Cu^{2+} (or Cu^{+}) ions from copper-bearing minerals into an aqueous H_2SO_4 solution, resulting in a copper-enriched leach solution (pregnant leach solution). However, the application of this technological cycle is not suitable for the processing of copper sulphide ores.

In the present study, the feed material is a copper sulphide concentrate (with chalcopyrite, $CuFeS_2$, as the principal mineral). In direct hydrochloride leaching of this concentrate, copper passes entirely into solution as monovalent copper chloride (CuCl), which, as is well known, provides favorable conditions for the precipitation of copper (I) oxide (Cu_2O) using sodium hydroxide.

The objective of this work is to analyze the optimal technological cycle for processing local sulphide copper concentrates in order to recover copper, iron, gold, and silver. This includes: direct hydrochloride leaching of chalcopyrite for copper recovery; two-stage hydrogen reduction of the oxide tailings formed during hydrochloride leaching for iron recovery; and cyanide leaching of the residual (secondary) tailings followed by traditional electrolysis of the solution, for the recovery of gold and silver.

Experimental methods. The concentrations of metal ions in solutions were measured using the atomic absorption spectroscopy (AAS) method. The contents of the major and minor components in solid residues were determined by chemical and emission–spectral analysis. The phase compositions of solid materials were studied by X-ray diffraction (XRD) analysis.

Discussion of the research results. At present, four main hydrometallurgical processing technologies are employed for copper ores: heap leaching, vat leaching, in-situ leaching, and agitated leaching. In addition, the method of leaching within the ore body itself, though still rarely applied, is also considered. The choice of a particular leaching technique for copper recovery from a given type of ore depends primarily on the copper content in the ore, its mineralogical composition, and the particle size of the constituent minerals [1] (Fig. 1). Furthermore, the geographical location of the deposit, climatic conditions, and economic factors may also influence the selection of the leaching method.

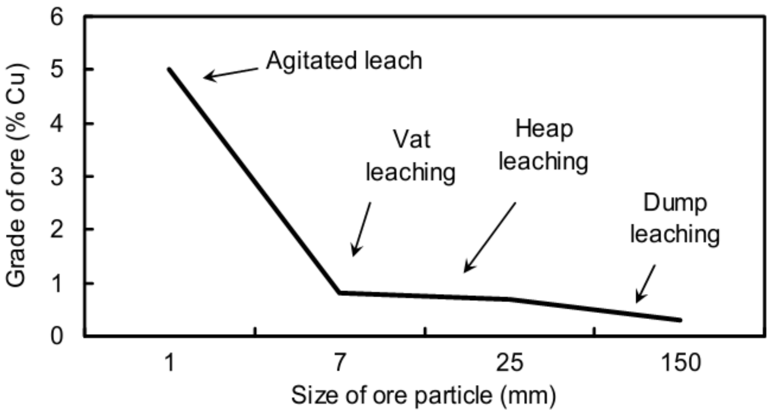

Fig. 1. Dependence of the copper leaching method on its content in the ore and on particle size

Heap leaching constitutes the majority of copper hydrometallurgical production. During both heap and dump leaching, the leaching solution percolates through the ore mass under the influence of gravity [2]. In the case of column leaching, the solution is forced through the ore, after which it is collected and processed to extract copper.

In both heap and dump leaching methods, non-sulphide copper minerals are leached using H_2SO_4:

$$CuO + H_2SO_4 \rightarrow Cu^{2+} + SO_4^{2-} + H_2O. \quad (1)$$

However, the leaching of sulphide minerals, in addition to H_2SO_4, also requires the presence of an oxidizing agent. With oxygen participation, the main reaction of copper sulfide leaching is as follows:

$$Cu_2S + 1/2O_2 + H_2SO_4 \rightarrow CuS + CuSO_4 + H_2O\ . \quad (2)$$

The heap leaching of sulphide ores can be enhanced by the participation of microorganisms. Bacteria, which naturally occur in the ore, act as catalysts during the leaching reactions. Their activity increases the reaction rate, thereby making the leaching duration of the ore economically viable.

On the other hand, experiments have shown that the rapid progress of sulphide leaching reactions requires the presence of Fe^{3+} ions. For example, in ores containing iron minerals such as pyrite (FeS), the Fe^{3+}ions oxidize the sulfur in the presence of oxidizing bacteria (a black oxidizing bacterium acting as a catalyst), releasing Fe^{2+}ions. These Fe^{2} ions are then rapidly re-oxidized to Fe^{3+}ions by oxygen and the same catalyst.

With the active participation of trivalent iron ions and bacteria, copper sulphides can be directly leached according to the following reactions:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 2SO_4^{2-} + 2H_2SO_4, \quad (3)$$

$$O_2 + 4Fe^{2+} + 4SO_4^{2-} + 2H_2SO_4 \rightarrow 4Fe^{3+} + 6SO_4^{2-} + 2H_2O, \quad (4)$$

$$Cu_2S + 10Fe^{3+} + 15SO_4^{2-} + 4H_2O \rightarrow 2Cu^{2+} + 10Fe^{2+} + 12SO_4^{2-} + 4H_2SO_4. \quad (5)$$

As can be seen, the Fe^{2+} ions formed in reaction (3) are subsequently re-oxidized according to reaction (4), making the process cyclic [3].

Microbial catalytic processes are most often attributed to bacteria of the genera Acidothiobacillus ferrooxidans, Leptospirillum ferriphilum oxidans, and Acidothiobacillus thiooxidans. Ambient temperature is a critical factor for their activity. For example, in the temperature range of 40-45^{0}C, bacteria of the genus Acidothiobacillus caldus dominate, whereas at temperatures above 60°C, Sulfolobus metallicus and Metallosphaera spp. prevail [4].

The optimal activity of the bacteria is supported under the following conditions:

a) pH of the leaching solution between 1.5 and 6.0 (optimal ≈ 2);

b) temperature from 5 to 45°C (optimal ≈ 30°C);

c) adequate O_2 supply to the reaction zone of the leaching sulphide ore, often provided through specially designed pipes using mild aeration [5].

The column leaching method is suitable for low-copper oxide (0.5-1% Cu) and carbonate ores, where the leaching kinetics is rapid, requiring a relatively short duration [6]. After the ore is processed for the corresponding period (typically 4-20 days), the copper-enriched solution is subjected to metal recovery.

Agitated leaching is widely applied for oxide minerals due to their high leaching kinetics (e.g., carbonates) and for ores with higher copper content (0.8-5% Cu). This method can also be used for reprocessing residues obtained from other leaching techniques. Currently, it is extensively employed by the African Copperbelt company, whose ores consistently contain cobalt [7, 8].

The use of sulfuric acid in the leaching of copper sulphide minerals is also necessitated by the need to decompose their crystalline structures, allowing copper to enter the solution as Cu^2 ions [9].

For the successful leaching of all copper sulfides, in addition to sulfuric acid, the presence of Fe^{3+}ions and molecular O_2 is required as oxidizing agents. Copper in the sulphide is oxidized by $Fe^{3+}$and dissolves into solution, whereby trivalent iron is reduced to divalent form, and the resulting Fe^{2+} cations are re-oxidized by O_2 back to Fe^{3+}.

In these interactions, the Fe(II)/Fe(III) redox pair operates catalytically (this occurs at elevated temperatures, where the sulfur-containing residue is converted to sulfate rather than elemental sulfur formed under ambient conditions).

The leaching of chalcopyrite occurs under oxidizing conditions and at high temperatures according to the following reactions:

$$2CuFeS_2 + 4Fe_2(SO_4)_3 \rightarrow 2Cu^{2+} + 2SO_4^{2-} + 10FeSO_4 + 4S, \quad (6)$$

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O, \quad (7)$$

$$2S + 3O_2 + 2H_2O \rightarrow 2H_2SO_4\,, \quad (8)$$

$$4CuFeS_2 + 17O_2 + 4H_2O \rightarrow 4Cu^{2+} + 4SO_4^{2-} + 2Fe_2O_3 + 4H_2SO_4. \quad (9)$$

Within the scope of this work, the hydrochloride leaching method tested is the most advanced (Fig. 2), as all operations are carried out in a closed cycle. The main active agent, copper (II) chloride ($CuCl_2$, introduced at the start of the cycle as $CuCl_2$ salt in an aqueous NaCl solution), is regenerated during the process according to the following reaction:

$$CuCl + 1/2Cl_2 = CuCl_2. \quad (10)$$

The chalcopyrite concentrate being processed (main component $CuFeS_2$) is loaded into a saturated aqueous solution of sodium chloride, where the chalcopyrite ($CuFeS_2$) decomposes under the action of copper (II) chloride ($CuCl_2$) and aerated oxygen, resulting in copper (I) chloride (CuCl) in solution, iron oxide (Fe_2O_3) as a solid residue, and elemental sulfur (on the solution surface):

$$CuFeS_2 + CuCl_2 + 3/4O_2 = 2CuCl + 1/2Fe_2O_3 + 2S. \quad (11)$$

The copper (II) chloride required for this reaction is prepared separately by reprocessing half of the copper (I) chloride solution obtained and purified from the leaching phase and residues, using industrial chlorine gas (at 85°C). Air is also bubbled through the solution.

The other half of the copper (I) chloride solution, purified from the leaching residues, is separately processed with industrial sodium hydroxide to obtain divalent copper oxide as a precipitate. The oxide precipitation occurs according to:

$$2CuCl + 2NaOH = Cu_2O + 2NaCl + H_2. \quad (12)$$

During the oxide precipitation stage, the aqueous solution of sodium chloride consumed in the leaching phase is simultaneously regenerated and returned to the concentrate leaching tank.

The copper oxide powder obtained, after washing and drying, is reduced with industrial hydrogen to produce metallic copper:

$$Cu_2O + H_2 = 2Cu + H_2O. \quad (13)$$

In an induction furnace, the metallic copper is then melted and cast to obtain copper of standard purity.

For the industrial chalcopyrite concentrate (-0.071 *mm*), the following optimal conditions were selected for hydro-chloride leaching:

- Leaching temperature: 85°C;
- Saturated aqueous solution of NaCl (30% NaCl);
- Duration: 12 hours, under continuous stirring and intensive aeration.

Under these conditions, the experimental results obtained from the industrial chalcopyrite concentrate (Table, Fig. 2) demonstrate that, on average, 99% of copper passes from the material into the solution (Table), which is a highly acceptable indicator.

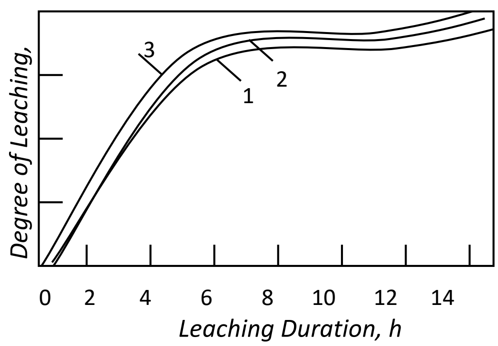

Fig. 2. The leaching curves of chalcopyrite concentrate.1 - 28,2% Cu, 2 - 26,5 %Cu, 3 - 28 %Cu

Table

Experimental results of industrial chalcopyrite concentrate leaching

Sample №	Cu, %	Conditions	Degree of Copper Extraction, %
Concentrate-1	28.2	85 °C, 10 h	98.8
Concentrate-2	26.5	85 °C, 12 h	99.1
Concentrate-3	28.0	85 °C, 14 h	99.2

The insoluble residue resulting from the leaching of copper concentrate-the slimes, which consist of chemical compounds of Fe_2O_3, Au, and Ag-is subjected to washing, drying, and preliminary recovery. The resulting magnetite slimes (Fe_3O_4, Au, Ag) undergo multi-stage magnetic separation, after which the oxide slimes (Au, Ag) are treated by cyanide leaching and electrowinning to produce a dore alloy (Au, Ag), while the recovery process of the magnetite concentrate yields iron powder.

The experimental data also indicate that the copper content in the tested concentrate has almost no effect on its leaching efficiency, which demonstrates the universality of the hydrometallurgical method.

In a liquid medium, the interactions between the solvent ($CuCl_2$) and the soluble mineral ($CuFeS_2$) are of a surface nature, determined by the fineness of the solid particles and the rate of mass transfer, the primary factor of which is the temperature of the solvent. In this case, 85°C provides sufficient conditions, as confirmed a priori by experimental methods. Higher temperatures could further accelerate the leaching process; however, intense vaporization of the solution at elevated temperatures may cause additional environmental pollution. Therefore, 85°C is accepted as the optimal temperature.

Conclusion. The hydrochloric leaching method ensures the direct and effective leaching of chalcopyrite concentrate. Using this method, the copper extraction rate can exceed 99%.

References

1. **Scheffel R.E.** Copper heap leach design and practice // Mineral Processing Pplant Design, Practice, and Control.- Littleton, CO: SME, 2002.- Vol. 2.- P. 1571-1605.
2. **Murr L.E.** Theory and practice of copper sulfide leaching in dumps and in-situ // Minerals Science and Engineering.- 1980.- № 12.- P. 121-189.
3. **Brierley C.L., Brierley J.A.** Bioheap processes - operational requirements and techniques // Copper Leaching, Solvent Extraction and Electrowinning Technology. - Littleton, CO: SME, 1999. - P. 17-27.

4. **Watling H.R.** The bioleaching of sulfide minerals with emphasis on copper sulfides: A review // Hydrometallurgy. – 2006.- № 84. - P. 81-108.
5. **Salomon-de-Friedberg H.** Design aspects of aeration in heap leaching // Randol Copper Hydromet. Roundtable.- *98* Golden.- CO: Randol International, 1998.- P.243-247.
6. **Zarate G., Saldıvar E., Rojes C., Nunez J.** Vat leach cycle optimisation at Anglo American Chile Mantos Blancos division // Cytec Solutions.- 2004.- № 10.- P. 4-5.
7. **Reolon M., Gazis T., Amos S.** Optimizing acid utilisation and metal recovery in African Cu/Co flowsheets // Hydrometallurgy Conference, Johannesburg, South Africa: Southern African Institute of Mining and Metallurgy.– Reolon, 2009.- P. 1-20.
8. Copper oxide agitated leaching on the African Copperbelt and possible heap leach application / **L. Roux, M. van Rooyen, E. Minnaar, et al** // Copper.- 2010.- Vol. 5: Hydrometallurgy Clausthal-Zellerfeld.- Germany: GDMB, 2010. - P. 1999 - 2016.
9. **Sherrit R., Pavlides A.G., Weekes B.L.** Design and commissioning of the Sepon copper pressure oxidation circuit // 1st Extractive Metallurgy Operators' Conference.-Victoria: Australasian Institute of Mining and Metallurgy, 2005.- P. 21-27.

Received on 24.11.2025.
Accepted for publication on 25.12.2025.

ԽԱԼԿՈՊԻՐԻՏԱՅԻՆ ԽՏԱՆՅՈՒԹԵՐԻ ՀԻԴՐՈՄԵՏԱԼՈՒՐԳԻԱԿԱՆ ՎԵՐԱՄՇԱԿՈՒՄԸ՝ ՊՂՆՁԻ, ՈՍԿՈՒ ԵՎ ԱՐԾԱԹԻ ԿՈՐԶՄԱՆ ՆՊԱՏԱԿՈՎ

Ա.Մ. Հովհաննիսյան, Դ.Գ. Վարդանյան

Ներկայացված են պղնձային խտանյութերի հիդրոմետալուրգիական եղանակով վերամշակման առանձնահատկությունները: Բերված են հանքանյութերի կույտային տարրալուծման, չաներում տարրալուծման և մանրէների ներգործությամբ տարրալուծման գործընթացների առանձնահատկությունները: Արտադրվող պղնձային խտանյութերում պղինձը հիմնականում հանդես է գալիս խալկոպիրիտի ($CuFeS_2$) և խալկոզինի (Cu_2S) տեսքով, իսկ երկաթը՝ պիրիտի (FeS_2) տեսքով: Ներկայացված են խտանյութի տարրալուծման օպտիմալ տեխնոլոգիական պայմանները՝ արժեքավոր մետաղների կորզման առավելագույն արդյունավետություն ապահովելու նպատակով: Ցույց է տրվել, որ մշակման համապատասխան տեխնոլոգիական սխեմայի ընտրությունը պետք է հիմնված լինի խառնուրդի հանքաքարային բաղադրության, համակցված մետաղական ֆազերի բաշխման և վերականգնելի բաղադրիչների կոնցենտրացիայի վրա:

Ծծմբով հարուստ պղնձային խտանյութերի դեպքում ամենաարդյունավետ մեթոդը համարվում է ուղղակի քլորիդային լվացումը, որը բնութագրվում է պղնձի լուծման բարձր արագությամբ, մեծ ընտրողականությամբ և բարենպաստ աշխատանքային պայմաններով: Օպտիմալ ռեժիմներում պղինձը ամբողջությամբ անցնում է լուծույթ՝ մեկարժեք պղնձի քլորիդի ձևով, որն այնուհետև վերամշակվում է՝ ստանալու համար բարձր մաքրությամբ մետաղական պղինձ:

Չլուծվող օքսիդային մնացորդներից երկաթի վերականգնումն իրականացվում է երկաստիճան հիդրոգենային վերականգնման վերահսկվող գործընթացով, որի արդյունքում ստացվում է արդյունաբերական կիրառման համար հարմար մետաղական երկաթի փոշի: Վերջնական օքսիդային պոչանքները՝ ոսկով և արծաթով հարստացված, ենթարկվում են ցիանիդային լվացման, այնուհետև՝ տեղակայման և էլեկտրաքիմիական մշակումների՝ ձեռք բերելու բարձրորակ Դորե համաձուլվածք:

Առաջարկվող ինտեգրված տեխնոլոգիական սխեման ապահովում է հումքի ամբողջական օգտագործում և բարձր ցուցանիշներ ինչպես բազային, այնպես էլ թանկարժեք մետաղների վերականգնման համար: Բացի այդ, քլորիդային լվացման փակ ցիկլի բնույթը և երկրորդային թափոնների նվազեցումը բարձրացնում են գործընթացի բնապահպանական անվտանգությունն ու կայունությունը:

Առանցքային բառեր. պղնձի սուլֆիդային խտանյութ, միներալային բաղադրություն, տարրալուծում, վերականգնում:

ГИДРОМЕТАЛЛУРГИЧЕСКАЯ ПЕРЕРАБОТКА ХАЛЬКОПИРИТОВЫХ КОНЦЕНТРАТОВ ДЛЯ ВЫДЕЛЕНИЯ МЕДИ, ЗОЛОТА И СЕРЕБРА

А.М. Оганесян, Д.Г. Варданян

Рассмотрены особенности гидрометаллургической переработки медных концентратов. Приведены характеристики процессов кучного, чанового и бактериального (био) выщелачивания. В промышленно производимых медных концентратах медь в основном присутствует в форме халькопирита ($CuFeS_2$) и халькозина (Cu_2S), а железо - в виде пирита (FeS_2). Представлены оптимальные технологические условия выщелачивания концентрата с целью обеспечения максимальной эффективности извлечения ценных металлов. Показано, что выбор соответствующей технологической схемы должен основываться на минералогическом составе сырья, распределении сопутствующих металлических фаз и концентрации извлекаемых компонентов.

Для серосодержащих медных концентратов наиболее эффективным методом является прямое хлоридное выщелачивание, которое характеризуется высокой скоростью растворения меди, высокой селективностью и благоприятными эксплуатационными условиями. В оптимальных режимах медь полностью переходит в раствор в форме одновалентного хлорида меди, который затем перерабатывается для получения высокочистой металлической меди.

Извлечение железа из нерастворимых оксидных остатков осуществляется посредством контролируемого двухстадийного водородного восстановления, в результате которого получают металлический железный порошок, пригодный для промышленного применения. Финальные оксидные хвосты, обогащённые золотом и

серебром, подвергаются цианидному выщелачиванию, после чего - осаждению и электрохимической обработке для получения высококачественного доре́-сплава.

Предлагаемая интегрированная технологическая схема обеспечивает комплексное использование сырья и высокие показатели извлечения как цветных, так и благородных металлов. Кроме того, замкнутый цикл хлоридного выщелачивания и снижение объёма вторичных отходов повышают экологическую безопасность и устойчивость процесса.

Ключевые слова**:** сульфидный медный концентрат, минералогический состав, выщелачивание, извлечение.